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FABRICATION OF HEAT PIPE COPPER MANIKIN

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METALS RESEARCH BRANCH

November 1989

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ABSTRACT

The U.S. Army Natick RD&E Center requested help from the Corrosion Science Team for their project on fabrication of a copper manikin to test insulating properties of textile materials. Sintering experiments were carried out to understand the mechanism of pore formation, the plasma spray process was explored as a means of forming the desired rough surface, and electrochemical measurements were made to assess the probability of galvanic corrosion between the copper felt and the electroformed copper in distilled water. The massive porosity formed during vacuum sintering was caused by thermal etching. Sintering in a hydrogen furnace eliminated the pore formation but caused a problem with the binder removal. A two stage sintering process using a vacuum furnace followed by a hydrogen furnace is suggested to alleviate both problems. The difference in corrosion potential between different types of copper in distilled water is not believed to be significant and no danger of hydrogen evolution is envisioned.

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INTRODUCTION

The Fiber and Fabric Technology Branch of the U.S. Army Natick RD&E Center (NRDEC) initiated a project to develop a copper manikin to test insulating properties of textile materials used for soldiers clothing. A contract was awarded to Thermo Electron, Inc. (TE) of Waltham, MA to build a manikin. The inside of the manikin was to have a rough surface that could act as a wicking surface for the heat pipe design concept. Thermo Electron, Inc. proceeded to design the manikin using vacuum sintering of copper particles, bonded with an organic binder, inside an electroformed hollow shape. During sintering, large pores developed making this process unacceptable. As an alternate approach, copper felt was used as a cathode to electroform the manikin parts to provide the interior wicking surface. However, they found a difference in electrochemical rest potential between the copper felt and the electroformed copper in distilled water. Consequently, they did not finish the construction of the manikin and requested termination of the contract. Following this development NRDEC sought the help from the Corrosion Science Team at the U.S. Army Materials Technology Laboratory (MTL) in solving the problems associated with fabrication of the copper manikin. At MTL, sintering experiments were carried out to understand the mechanism of pore formation, the plasma spray process was explored as a means of forming the desired rough surface, and electrochemical measurements were made to assess the probability of galvanic corrosion between the copper felt and the electroformed copper in distilled water. This report describes the work done at MTL on this project.

In a heat pipe, surface tension driven mass transfer of the heat exchange medium takes place from the lower end of the pipe to the upper end of the pipe. A rough surface that can act as a wick is necessary for this transfer to take place. At the upper end of the pipe the fluid is heated by a heating element which vaporizes the liquid. The condensing vapor uniformly distributes the heat and the liquid then accumulates at the bottom allowing the cycle to repeat. This phenomenon offers more uniform temperature distribution throughout the pipe than many other techniques. However, for the heat pipe to function efficiently, a rough surface with interconnected porosity is necessary. The approach TE used was to sinter -30 + 100 mesh spherical oxygen free high conductivity (OFHC) copper powder with a 94% dimethyl acetamide -6% hydroxyethyl cellulose binder to the inside of a spun OFHC copper beaker, ~ 6 in. diameter; the inside surface was painted with the binder and the copper powder was spread and shaken to distribute it evenly. The beaker was then placed in a vacuum furnace at 1000°C for 1 hour at 3 mTorr. During sintering, all the cellulose burnt off and a good metallurgical bond was established between the powder and the substrate. However, an unacceptable large amount of porosity was also evident on the exterior surface of the beaker. Alternatively, TE explored the use of copper felt as a wicking surface. The copper felt pad was available as an off-the-shelf item. Electroforming was carried out in an electrolyte containing CuSO_4 and additives including brighteners, using the copper felt as the cathode. All but one surface of the cathode were sealed with a high density wax to restrict the copper deposition to only that surface. Electrochemical rest potential measurements were carried out in double distilled deionized water. They measured a potential difference of 100 mV at a current density of 50 mA/sq. in. They attributed this difference in potential to the difference in chemistry of the copper felt and the electrodeposited copper. They further postulated a hydrogen evolution cathodic reaction. Since the presence of any gas in the heat pipe could severely hamper the efficiency of the operation, any possibility of hydrogen evolution is a cause for major concern. Following these findings, TE recommended to NRDEC that the copper heat pipe concept for the manikin was not feasible and the project should be terminated. NRDEC personnel contacted the Corrosion Science Team at MTL for help on this project in light of these developments. They specifically requested our opinion on the following:

1. What is the mechanism of pore formation during sintering?
2. Is the galvanic corrosion problem postulated by Thermo Electron, Inc. a real one? How much hydrogen would be generated, and can this be avoided?
3. Are there any alternative processes to avoid these problems?
4. What kinds of problems will be encountered during welding of copper?

NRDEC transferred funds for this work to answer these questions. This report describes the work accomplished and the recommendations made.

EXPERIMENTAL RESULTS AND DISCUSSION

The original beaker was cut at one of the pores and examined under a scanning electron microscope (SEM). Figure 1 shows an area around these pores at 500X. The absence of dendrites in the microstructures indicates melting has not occurred. Since the specimen was slowly cooled in the furnace, a dendritic structure was expected. In view of the very low vacuum at a fairly high temperature, the mechanism of pore formation is believed to be due to thermal etching (grooving). This is evident in Figure 2 which shows a very smooth surface at a substrate grain boundary where the material has evaporated. Based on this finding, it was decided to carry out a sintering experiment in a hydrogen furnace. The same procedure as described by Thermo Electron, Inc. was followed to bind the copper powder to OFHC copper specimens about 1 x 2 in. in size. According to this procedure, the specimens were sand blasted with 100 mesh grit to provide the surface roughness needed for adhesion. The samples were then chemically etched in a solution of 50% nitric and 50% phosphoric acids to promote adhesion by removing any surface films present. The samples were thoroughly rinsed with water to remove any trace of acids. The binder, a mixture of 6% hydroxyethyl cellulose and 94% dimethyl acetamide, was applied using a fine camel hair paint brush. A second coat was applied after the first coat was completely dry. The sample to be coated was placed in the copper powder and shaken to uniformly spread the copper powder on the surface. Table 1 shows the processing time and temperatures for the samples tested. For sample A, after 10 minutes at 700°C in the hydrogen furnace, sintering was not complete. Hence, it was given another 10 minutes at 850°C which was also deemed inadequate. An additional 30 minutes at 900°C proved to be sufficient for the desired structure. Accordingly, a second sample, B, was tried at 900°C for 30 minutes but was deemed unacceptable. An additional 60 minutes were given at 950°C to achieve the desired bonding of the copper powder to the specimen, as shown in Figure 3. Sample C was sintered at 1000°C for 60 minutes resulting in an acceptable coating. It was recoated to increase the coating thickness and resintered for another 60 minutes. The resultant coating was acceptable. In general, the hydrogen furnace was very beneficial in avoiding any oxidation of the copper specimens. The problem, however, was removal of the binder. The cellulose binder reacted with hydrogen differently for every run and was not readily decomposed in the hydrogen furnace making sintering difficult. Furthermore, it was not related to either the time or the temperature of the experiment. Figure 3 shows the pictures of these samples after sintering. An alternate approach of decreasing the sintering time to 10 minutes, as compared to the 1 hour followed by Thermo Electron, Inc., was tried. Sample D was sintered in a vacuum furnace at 1000°C for 10 minutes. Good adhesion was obtained and no porosity was formed. However, the surface tarnished due to slight oxidation. The vacuum in this case was 100 mTorr, considerably less than the 3 mTorr vacuum used by TE. Another approach was attempted in which a specimen was first sintered in the vacuum furnace for 30 minutes and then sintered in the hydrogen furnace. However, during the vacuum sintering the furnace broke and the experiment was never completed.

The vacuum furnace was never repaired. Hence, this experiment was not fully carried out. This procedure, however, offers the optimum approach to avoid the problems of porosity or oxidation. Samples E and F were tried at 950°C to confirm the sintering temperature of 950°C or above.

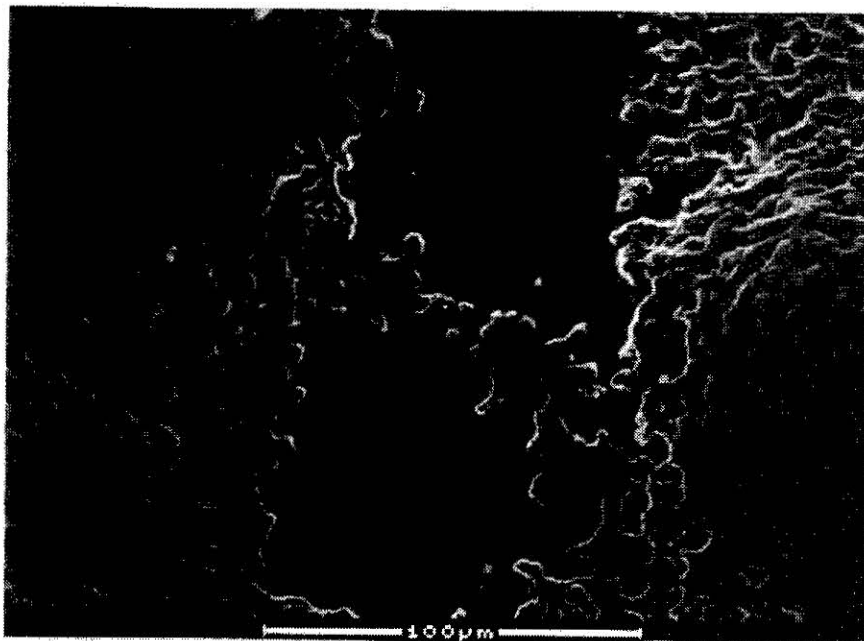


Figure 1. SEM picture of the copper beaker in an area near massive pores - 20 kV, mag. 500X. Notice the absence of any evidence of melting such as a dendritic structure.

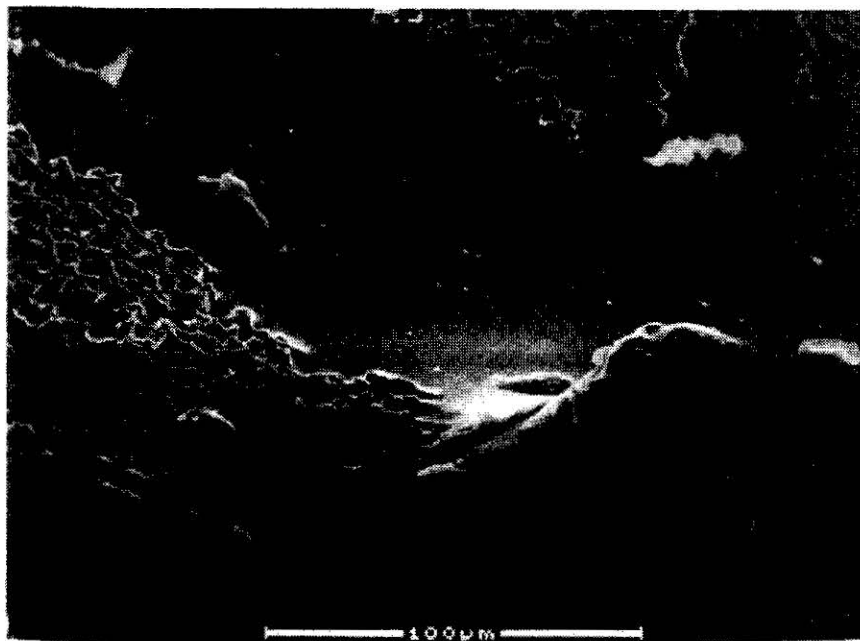


Figure 2. SEM picture of the copper beaker in an area where pore formation has been initiated but not completed - 20 kV, mag. 500X. Notice the smooth surface of the substrate grain boundary.

Table 1. SINTERING PARAMETERS

Sample	Temperature (°C)	Furnace	Time (min.)
A	700	Hydrogen	10
A	859	Hydrogen	10
A	900	Hydrogen	30
B	900	Hydrogen	30
B	950	Hydrogen	60
C	1000	Hydrogen	60
C	1000	Hydrogen	60 2nd coat
D	1000	Vacuum	10
E	950	Hydrogen	30
E	950	Hydrogen	30 2nd coat
F	950	Hydrogen	60

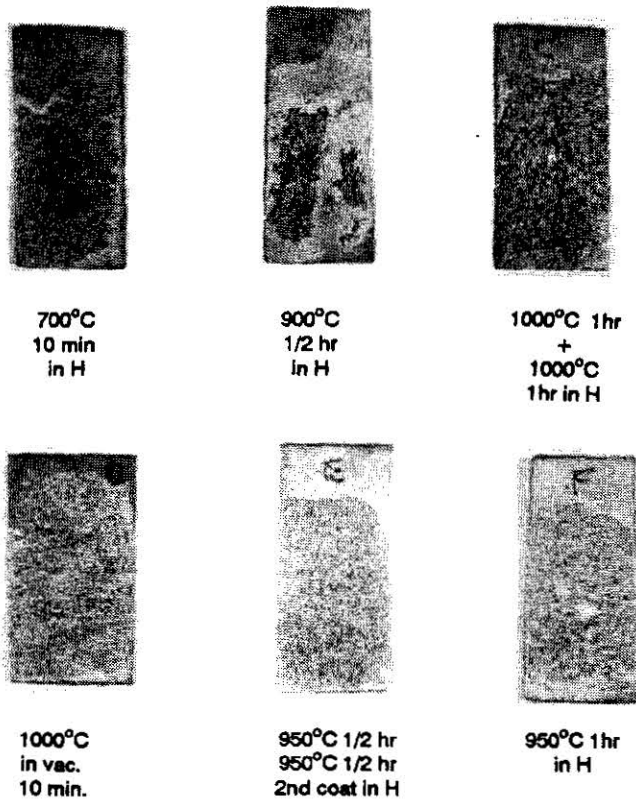


Figure 3. Pictures of the sintered OFHC specimens.

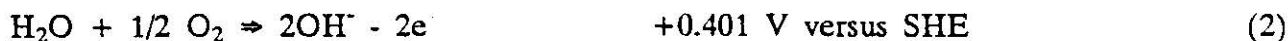
Based on these sintering experiments, it was concluded that hydrogen sintering yields an acceptable coating with no oxidation, but presents a problem with the binder removal. Vacuum sintering, on the other hand, removes the binder, but tarnishes copper and causes thermal etching. Therefore, a combination of both is desirable. A two stage process 10 minutes in a vacuum furnace to remove the binder and to partially sinter the powder, followed by 40 minutes in a hydrogen furnace to complete the sintering without tarnishing or thermal etching, is believed to be optimum.

An alternate approach using a plasma spray process to produce a rough surface with interconnected porosity was tried. Two grades of powder were provided by NRDEC. Grade 46 HP was -30 + 100 mesh, whereas Grade 61 was -100 mesh. The plasma spray parameters for spraying this size copper powder on a copper substrate were not readily available. After consultations with the service engineering department of Metco, Inc., the parameters shown in Table 2 were employed. The specimens were grit-blasted and preheated to 200°C. Grade 46 HP powder did not adhere to the substrate. Grade 61 resulted in good adhesion due to its fine size and was considered successful. One substrate was also pickled in 50% H₂SO₄, but the coating did not adhere. Hence, pickling was never tried again. Figure 4, photomicrographs of the cross section of a sample processed in this manner, shows that the coating is full of porosity. Most of the porosity is interconnected in the direction parallel to the surface. For better wicking properties, however, interconnected porosity in the direction perpendicular to the surface is also desired. This sample was provided to NRDEC for evaluating the wicking properties. According to Ms. Seashultz, some wicking was observed but was not adequate. Under the present deposition conditions, the plasma spray process, therefore, does not provide a viable alternative.

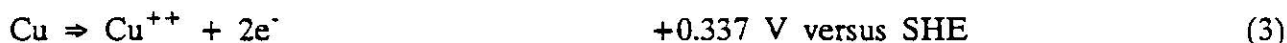
Table 2. PLASMA SPRAY PARAMETERS

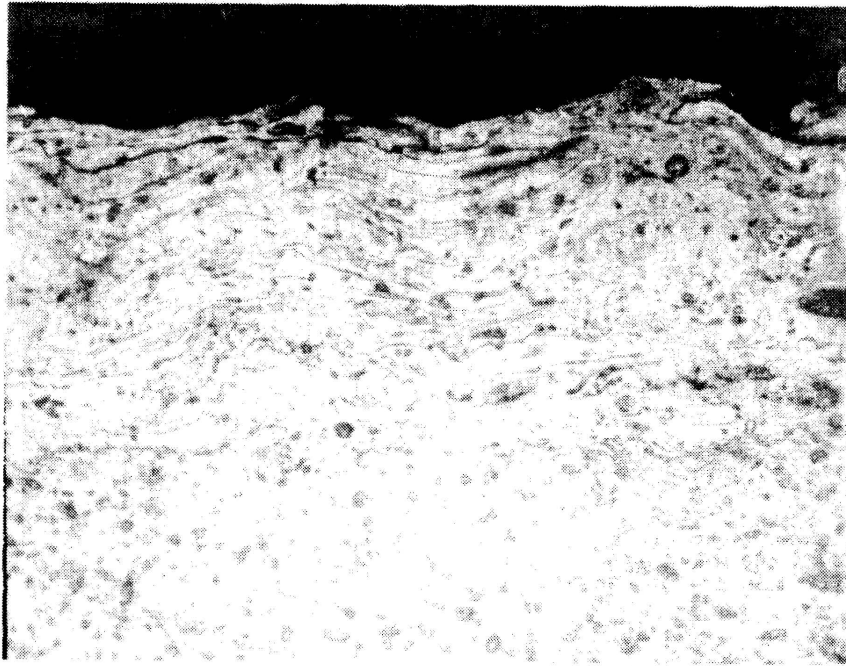
Nozzle	GH
Powder Port	#1
Primary Gas	Argon
Flow	150#
Secondary Gas	Hydrogen
Flow	5#
Amperage	500
Voltage	60 to 70
Spraying Distance	4 to 6 in.

Corrosion potential measurements were carried out in deionized distilled water on the electroformed copper on copper felt. During the test, a considerable amount of bleeding of red chemicals was observed. This may have been some kind of a dye used in the sealing wax. The corrosion potential measurements conducted after 5 minutes and 24 hours in water are listed in Table 3. These values show that the corrosion potential did not change significantly after 24 hours of immersion. Electroplated copper is more anodic than pure copper, whereas the copper felt is more cathodic than pure copper. All the values are more cathodic than hydrogen, the implication being that the hydrogen evolution reaction is not a possible cathodic reaction for this galvanic corrosion couple. The possible cathodic reactions are:

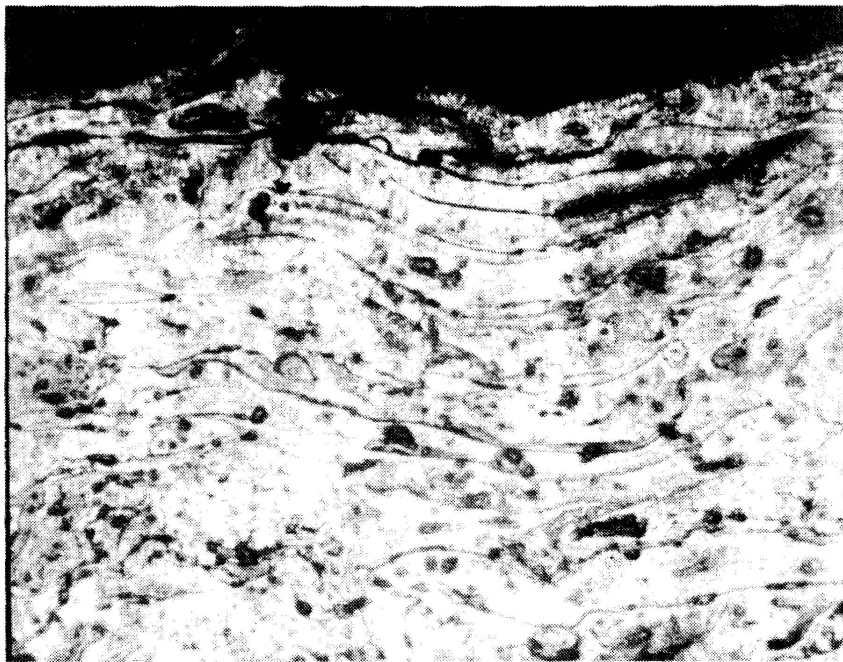


The possible anodic reaction is:





(a) mag. 150X



(b) mag. 300X

Figure 4. Photomicrographs of the plasma-sprayed copper specimens.
Notice the limited amount of interconnected porous structure of the deposit.

Table 3. CORROSION POTENTIAL MEASUREMENTS (VOLTS VERSUS SCE)

Material	Time After Immersion		
	1 minute	10 minutes	24 hours
Copper Felt Pad	+0.009	+0.010	+0.007
Pure Copper*	—	+0.095	—
Electroformed Cu	-0.068	-0.070	-0.078
Hydrogen*	—	-0.242	—

*Indicates reference values from Corrosion Engineering by Fontana and Greene, published by McGraw-Hill, Inc., p. 31, 1967, and converted to SCE scale.

As can be seen from the above reactions, gas evolution is not a concern in this case. Neither of the possible cathodic reactions involve hydrogen evolution. Furthermore, oxygen would have to be available for the cathodic reaction to proceed. Reaction 1 requires hydrogen ion to proceed and, hence, the pH of the solution would have to be acidic. Reaction 2, on the other hand, would proceed in a basic solution. In either case, oxygen depletion is involved. A supply of oxygen would be required for the corrosion reaction to take place. If the system is sealed and closed to the exterior, oxygen will not be readily available. In deionized double distilled water the supply of hydrogen or hydroxyl ions is very limited. Accordingly, very little corrosion is expected. Furthermore, due to an extremely low conductivity of deionized double distilled water, the corrosion current, if any, is expected to be extremely low. It is conceivable that the electrolyte from the plating operation may get trapped in the copper felt and contaminate the distilled water. If so, a frequent change of water used for heat exchange in the initial stages of operation is recommended. If this is not possible, perhaps a thorough washing of the heat pipe prior to the final assembly should be considered.

CONCLUSIONS AND RECOMMENDATIONS

1. Massive porosity observed by Thermo Electron, Inc. during vacuum sintering of copper powder bonded to the electroformed copper with a cellulose-based binder was due to thermal etching (evaporation of the metal at the grain boundaries).
2. Thermal etching during sintering can be avoided by sintering in a hydrogen furnace. However, complete removal of the binder during sintering could be a major problem.
3. A two stage sintering process, 10 minutes in a vacuum furnace followed by 40 minutes in a hydrogen furnace at 1000°C, may avoid problems with massive porosity, binder removal, and tarnishing.
4. The plasma spray process provides a surface with limited wicking ability for heat tube operation and is not as good as the sintered surface or the felt.
5. The corrosion potential difference observed between the copper felt and the electroformed copper specimens in deionized distilled water is not expected to present any major gas evolution problems in service. The cathodic reaction presents oxygen depletion and not hydrogen evolution. A solution pH level above 7 for the heat transfer medium should be avoided to minimize corrosion of the copper parts and formation of copper hydroxides.

6. Electroforming on the copper felt pad is a viable option, but care must be taken to seal the surface prior to immersion in the electrolyte to avoid trapping the liquid in the felt. This may be more difficult than the sintering option.

7. Welding of copper is generally not recommended. The joining of copper parts is usually carried out by brazing. Brazing alloys will most likely have a different corrosion potential than copper. This is not expected to be a major problem because of the extremely low conductivity of deionized double-distilled water. Zinc-containing brazing alloys, however, should be avoided. Zinc is more anodic to copper, will corrode preferentially, and can lead to hydrogen evolution. Silver-brazing alloys will avoid hydrogen evolution. Accordingly, silver-brazing alloys are recommended for any brazing of copper manikin parts.

8. Based on the work carried out to date, copper powder glued with the cellulose binder, followed by a two-stage sintering process, appears to be the most viable option. A close monitoring of the metallurgical work by the future contractor is recommended to minimize any future technical problems related to metallurgy of the copper manikin forming process.

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Key Words

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Heat pipes
Sintering

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illus-tables

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